Rapid Determination of Thorium by Fluoride Titration Using Some Chromotropic Azo Dyes

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Thorium nitrate has been employed by many workers as a reagent for the volumetric analysis of fluoride. Willard and Winter[1] used alizarin sulfonate as indicator in the titration of fluorine with thorium nitrate. This method for the determination of fluorine in minerals and rocks has undergone many modifications in the hands of many workers[2]. Menis and co-workers[3] used alizarin red-S for the titration of fluoride by an automatic spectrophotometric device. Gurev and Ioffe[4] employed the thorium-alizarin red-S lake for the photometric determination of fluorine in zinc concentrates and electrolytes. This dye found application in the determination of this halogen by column chromatography with cellulose supported with alizarin red-S[5]. This thorium-alizarin sulfonate method has also been used by Guntz and Arene[6] for the colorimetric determination of fluorine in waters. Organic fluorine has also been determination by this method by Musgrave and Smith[7] and later the method was modified by Stross and coworkers[8] and also by Ellis and Musgrave[9]. Milton and Liddel[10] employed solochrome Brilliant Blue B. S. as indicator for the estimation of fluorine. Willard and Horton[11] made a comparative study on the use of many indicators for the titration of fluoride with thorium nitrate and showed that purpurin sulfonate and alizarin red-S gave reproducible results. Banerjee[12] used his dye SPADNS as indicator for such titration. The present author employed three dyes: SNADNS-4, di-SNADNS-4 and nitroso-SNADNS-4 for the determination of fluorine present in fluorides and rocks[13].

The reversed procedure, i. e., titration of thorium with a soluble fluoride in presence of a metal indicator is also feasible. Banerjee[14] carried out such a titration using SPADNS dye. The present paper describes a method for the titrimetric determination of thorium with sodium fluoride using three chromotropic azo dyes: nitroso-SNADNS-4, SNADNS-6[15] and CHPADNS[16], prepared from 1-naphthylamine-4-sulfonic acid, 1-naphthylamine-6-sulfonic acid and *p*-aminosalicylic acid respectively. The dyes form pink to violet complexes with thorium, which are decomposed by the addition of a standard fluoride solution resulting in the liberation of the free dyes showing a marked color change at the end point.

Experimental

Reagents and Chemicals.—*Sodium Fluoride.*—A stock solution was prepared from Merck's analytical grade sodium fluoride, previously dried at 120°C to constant weight.

Thorium Nitrate.—A thorium nitrate solution of strength 0.0128 M was prepared from thorium nitrate tetrahydrate (E. M.) by standardising gravimetrically with oxalic acid and phenyl acetic acid.

Dye Solution.—The dyes were prepared by following methods previously described[15,16]. A 0.1% solution of the dyes was used.

TABLE I. EFFECT OF pH ON THE TITRATION
NaF = 0.0526 M

Th taken mg.	pH	Th found (mg.) with the dyes		
		Nitroso-SNADNS-4	SNADNS-6	CHPADNS
14.85	1.81	13.20	12.81	12.63
	2.01	13.51	13.45	13.52
	2.25	13.92	13.86	13.94
	2.43	14.84	14.82	14.83
	2.62	14.86	14.83	14.84
	2.83	14.84	14.86	14.86
	3.22	14.75	14.72	14.74

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TABLE II. DETERMINATION OF THORIUM WITH FLUORIDE

Th taken mg.	Volume of 0.0263 M NaF				
	Theoretical ml.	Actually required using the dyes			
		Nitroso-SNADNS-4 ml.	SNADNS-6 ml.	CHPADNS ml.	Alizarin-S ml.
43.07	28.24	28.19	28.17	28.18	28.17
31.19	20.45	20.42	20.40	20.43	20.41
29.70	19.47	19.48	19.45	19.47	19.43
23.76	15.58	15.60	15.59	15.61	15.57
11.88	7.79	7.78	7.76	7.80	7.80
2.97	1.95	1.98	1.94	1.96	1.93
1.49	0.98	0.96	1.00	0.94	0.95

Buffer Solution.—Standard acetate buffer mixtures of different pH were prepared as usual.

Starch Solution.—A 5% starch solution was prepared when required.

Optimum Conditions for the Determination of Thorium.—*Hydrogen Ion Concentration.*—Titration of thorium was carried out in solutions having different pH, adjusted by 0.01 N hydrochloric acid, sodium hydroxide or acetate buffer. It was observed that a pH range from 2.4 to 2.8 was more or less suitable for estimation with these dyes. (Table-I).

Concentration of the Dyes.—A. half ml. of 0.1% dye solution was sufficient to give good end points with smaller amounts thorium in 50 ml. volume.

Concentration of Thorium Solution.—Reproducible results were obtained when very dilute solutions of thorium were titrated. The end point becomes obscure and a considerable amount of the indicator is absorbed by the increased amount of thorium fluoride precipitate. The quantity of thorium present should not be more than 50 mg. per 50 ml.

Starch Solution.—A 5 ml. portion of 5% freshly prepared starch solution should be added per 50 ml. solution to reduce the precipitation of thorium fluoride, acting as a protective colloid[8].

Volume of Titrating Solution.—In order to find out the effect of dilution of the volume of the titrating solution on the end point, titrations were carried out by varying the final volume of the solution keeping all other things constant. It was found that titration was best done in 40~50 ml. volume.

Temperature.—The titration is to be carried out at room temperature. At higher temperature the end point became indistinct.

Analytical Procedure.—An aliquot quantity of thorium nitrate solution was taken in a 250 ml. Erlnmeyer flask to which was added 0.5 ml. of the indicator, the mixture was diluted to 40 ml. the pH was adjusted to 2.5 with 0.01 N sodium hydroxide or hydrochloric acid, 5 ml. of starch solution were added and the volume was finally made up to 50 ml. The titration was carried out rapidly with the standard sodium fluoride solution till the end point was attained. Blank titrations were also carried out side by side. Titration should be completed quickly as the efficacy of the starch solution is soon lost. At the end point the color of the solution with nitroso-SNADNS-4, changed from reddish-pink to yellow, with SNADNS-6 the change was from pinkish-blue to pink and with CHPADNS the color changed from pinkish-violet to red. The end point with nitroso-SNADNS-4 was very sharp and distinct. Some of the representative data given in Table II, show that the method is stoichiometric up to about 50 mg. of thorium, within the limits of experimental error. The results have been compared with those obtained by the use of alizarin red-S indicator at pH 2.9~3 and the results were found to agree favorably.

Determination of Thorium in Micro Quantities. The procedure for titrating microgram amounts of thorium was the same as before, excepting that a micro-burette, more dilute solutions of the fluoride and thorium nitrate and 0.5 ml. of 0.05% dye solution per 50 ml. final volume, were used. The end points were sharper in this titration as the bulk of thorium fluoride formed was small. The data recorded in Table III, indicate that as low as 3.8 μg. of thorium per 50 ml. may be determined using these dyes with fair accuracy.

TABLE III. MICRO-TITRATION OF THORIUM WITH FLUORIDE

Th taken μg.	Th found in μg. (NaF=0.0013 M)		
	Nitroso-SNADNS-4	SNADNS-6	CHPADNS
22.88	22.90	22.86	22.89
15.26	15.22	15.19	15.21
11.44	11.41	11.40	11.38
7.63	7.60	7.60	7.62
3.81	3.78	3.74	3.76

Effect of Various Ions on the Determination.—Possible interference in this determination was investigated. The ions that complex thorium or the dyes and also those which react with fluoride, interfere strongly. The elements which caused interference are as follows: lead, mercury(I), alkaline earth metals, iron, tin, manganese, magnesium, cerium, rare earth elements, zirconium, phosphate, borate, oxalate, tartrate and citrate. Determination could be carried out in the presence of other elements like copper, cadmium, aluminum, beryllium, zinc, mercury(II), cobalt, nickel, sodium and potassium. The results have been placed in Table IV.

TABLE IV. DETERMINATION OF THORIUM IN PRESENCE OF DIVERSE IONS

Th taken = 8.91 mg. = 5.84 ml. of 0.0263 M NaF

Elements	Amount mg.	Titre value (ml.) with		
		Nitroso-SNADNS-4	SNADNS-6	CHPADNS
Na	12.84	5.88	5.81	5.89
K	13.16	5.87	5.88	5.86
Cu	5.21	5.80	5.79	5.80
Cd	9.32	5.89	5.80	5.88
Al	6.03	5.81	5.78	5.80
Be	5.71	5.80	5.79	5.79
Zn	8.72	5.82	5.88	5.81
Hg(II)	4.32	5.83	5.80	5.86
Co	8.13	5.80	5.81	5.78
Ni	6.04	5.81	5.79	5.80

Summary

The thorium-chromotropic azo dye complexes are found to be fast-reacting with fluorides, in which exchange of dye molecule for fluoride ion takes place. The colored thorium-dye complexes are thereby decomposed with the liberation of the free dye and formation of thorium fluoride. The color changes at the end point enable visual comparison. Three dyes: nitroso-SNADNS-4, SNADNS-6 and CHPADNS have been used here as thorium complexing agents or indicators. The color change with the nitroso-SNADNS-4 at the end point is very sharp. Titrations are best carried out at pH range 2.4~2.8 and thorium present should not be more than 50 mg. per 50 ml. solution. With the increased precipitation of thorium fluoride the dyes are adsorbed in the precipitate and the end point becomes more obscured. Microgram amounts of thorium may also be determined by this method. A large number of cations and anions interfere in the process, of which the most important are: iron, cerium, rare earth elements, alkaline earth elements, phosphates, borates, oxalates, tartrates and citrates. This method is best applicable to thorium solutions from which the interfering elements have been removed.

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